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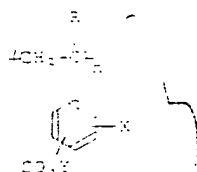
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(54) Process for production of chloroprene rubber

The invention concerns a process for preparing chloroprene rubber with minimal tendency to contamination of metal forms, characterized by the fact that chloroprene, or a mixture of chloroprene with a monomer suitable for copolymerization with chloroprene, in a proportion of up to 50%, based on the chloroprene, is polymerized in an alkaline aqueous emulsion in the presence of 0.5 to 5% by weight of a rosin acid derivative and 0.1 to 10% by weight polystyrenesulfonic acid or a derivative of it having the general formula I



in which R is a hydrogen atom or a lower alkyl group, X is a hydrogen atom, a lower alkyl group, a halogen atom, or a hydroxyl group, and Y is a hydrogen, potassium or sodium atom, or a quaternary ammonium group and n is an integer from 10 to 1000.

Our reference: S 476 (DV/ko)

16 June 1983

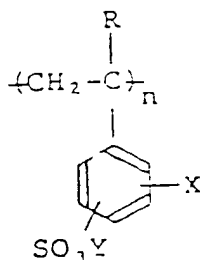
Case: 8168

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"Process for producing chloroprene rubber"

Patent Claims

1. Process for producing chloroprene rubber, characterized by the fact that chloroprene, or a mixture of chloroprene with a monomer suitable for copolymerization with chloroprene, in a proportion of up to 50%, based on the chloroprene, is polymerized in an alkaline aqueous emulsion in the presence of 0.5 to 5% by weight of a rosin acid derivative and 0.1 to 10% by weight polystyrenesulfonic acid or a derivative of it having the general formula I



in which

R is a hydrogen atom or a lower alkyl group,

X is a hydrogen atom, a lower alkyl group, a halogen atom, or a hydroxyl group, and

Y is a hydrogen, potassium or sodium atom, or a quaternary ammonium group and

n is an integer from 10 to 20,000.

2. Process according to Claim 1, characterized by the fact that the rosin acid derivative is present in a proportion of 1.0 to 3.0 percent by weight.

3. Process according to Claim 1, characterized by the fact that the polystyrenesulfonic acid or a derivative of it is present in a proportion of 1.0 to 5.0 percent by weight.
4. Process according to Claim 1, characterized by the fact that the mixture of chloroprene with the monomer also contains a molecular-weight-modifying agent and a radical initiator.
5. Process according to Claim 1, characterized by the fact that the monomer added to the chloroprene is 1-chlorobutadiene, 2,3-dichlorobutadiene, butadiene, 2-cyanobutadiene, styrene, acrylonitrile, alkyl methacrylate or alkyl acrylate.
6. Process according to Claim 1, characterized by the fact that the polystyrenesulfonic acid or its derivative is poly-p-styrenesulfonic acid or its sodium, potassium or quaternary ammonium salt, poly- α -methyl-p-styrenesulfonic acid sodium salt, or poly-o-chloro-p-styrenesulfonic acid with a mean degree of polymerization of 50 to 1000.

The invention concerns a process for producing chloroprene rubber with a minimal tendency toward formation of contaminants on the metal form (called metal form contamination in the following) used for compression molding and vulcanizing of chloroprene.

Chloroprene rubber is normally mixed with additives such as vulcanizing agents, vulcanizing aids, agents to protect against aging and fatigue, fillers, and plasticizers to attain the properties needed for practical use, such as high elasticity, high strength, and stability; then molded in a compression mold, and finally vulcanized.

If the process steps of compression molding and vulcanization of are carried out in a metal mold, using chloroprene and the usual rubber chemicals and additives, the additives contained in the mix can come to the surface and contaminate the metal mold. Spots continue to adhere to the mold even after the vulcanized material has been removed. On repeated use of the metal forms, the contaminants increase, resulting in the vulcanized rubber products having surface defects such as reduced gloss and roughening of the surface.

The forms must be cleaned often to remove the spots, in order to prevent defects at the surface of the vulcanized rubber products. That necessarily makes the process less economical. One measure for solving the problem of metal form contaminants is described in Japanese Laid-Open Patent Application 37118/74. This patent discloses a chloroprene rubber having improved properties with respect to metal form contamination through polymerizing chloroprene, with a degree of polymerization of at least 60%, in the presence of certain proportions of rosin soaps, an alkali metal salt of a higher saturated or unsaturated fatty acid and a sodium salt of a condensation product of formaldehyde and naphthalene sulfonic acid.

In contrast to the state of the technology described, the process according to the invention provides a chloroprene rubber having a very low tendency to contaminate the metal forms.

Thus the invention concerns the object characterized in the Claims.

The expression "lower alkyl group" means, preferably, an alkyl group with 1 to 8 carbon atoms.

A process for emulsion polymerization of chloroprene has since been described in Japanese laid-open patent application 40311/75. This process uses styrenesulfonic acid or a derivative of it along with an emulsifier such as rosin acid derivative. The styrenesulfonic acid, and its derivatives, used according to the patent, are, however, monomers and not polymerized compounds, with which the improved effect with respect to metal form contamination

obtained by the process of the invention cannot be expected.

The rosin derivatives used in the process according to the invention can, in general, be those commonly used in polymerization of chloroprene. Examples of these are undenatured colophonium, disproportionated colophonium, hydrogenated colophonium, and their alkali metal salts. As noted above, they are used at 0.5 to 5 percent by weight, preferably 1.0 to 3.0 percent by weight, based on the amount of chloroprene or of the mixture of chloroprene with the monomers suitable for copolymerization with chloroprene. If the proportion is less than 0.5 percent by weight the emulsion is less stable. If the proportion is greater than 5 percent by weight, contaminants can appear more easily on the metal form.

Examples of the polystyrenesulfonic acids and their derivatives used according to the invention are: poly-p-styrenesulfonic acid and its sodium, potassium and quaternary ammonium salts; poly- α -methylstyrenesulfonic acid sodium salt; and poly-o-chlorostyrenesulfonic acid having a mean degree of polymerization of 10 to 20,000, preferably 50 to 1000, in proportions of 0.1 to 10 percent by weight, preferably 1 to 5 percent by weight, based on the amount of chloroprene or of the mixture of chloroprene with the monomers suitable for copolymerization with chloroprene. If the proportion is below 0.1 percent by weight, the desired inhibition of metal form contamination is decreased; but proportions greater than 10 percent by weight should be avoided because then the chloroprene latices obtained are too viscous.

Depending on the conditions, higher saturated or unsaturated fatty acids such as stearic or oleic acid can be used with the previously mentioned rubber additives.

According to the invention, the polymerization can be carried out using the usual emulsion polymerization process, except that the proportions noted above must be maintained. The chloroprene can be used alone or, if necessary, in a mixture with up to 50 percent by weight of a monomer suitable for copolymerizing with chloroprene, such as 1-chlorobutadiene, 2,3-dichlorobutadiene, butadiene, 2-cyanobutadiene, styrene, acrylonitrile, alkyl methacrylate and alkyl acrylate.

Known modifying agents such as alkyl mercaptan and alkylxanthogen disulfide can be used as molecular-weight-modifying agents. Examples of radical initiators are potassium persulfate and alkyl hydroperoxide.

The polymerization should be carried out at temperatures of 0 to 100 °C, preferably 5 to 60 °C. The reaction should be continued in the presence of the stated proportions of the

compounds mentioned above until the conversion is at least 60%. Then polymerization is terminated by addition of one of the usual polymerization inhibitors such as tert-butylcatechol or phenothiazine.

After termination of the polymerization reaction, unreacted monomers are removed, especially by treatment at reduced pressure and elevated temperature. The polychloroprene latex produced in this manner is then cooled, coagulated, washed with water, and dried to obtain the solid chloroprene rubber.

The following examples explain the invention. 'Parts' refer to weight of not otherwise stated.

Example 1

Chloroprene, which contains 2,3-dichloro-1,3-butadiene and the compounds listed in Table 1, below, is placed into a 10-liter autoclave equipped with a stirrer. Polymerization is done under nitrogen at 40 °C with continuous feed of a 0.5% aqueous solution of potassium persulfate. After 70% conversion, the polymerization reaction is terminated by adding an emulsion of 0.01 parts each of tert-butylcatechol and phenothiazine. Unreacted monomers are removed by flash distillation.

The latex produced is adjusted to pH 5.8 with a 10% solution of acetic acid in water. The polymer is separated with a freezing roller, then washed with water and dried to give solid chloroprene rubber.

Table 1

Polymer number	I	II	III	IV	V	VI	VII	VIII
Chloroprene	95	95	95	90	95	95	95	95
Styrene	-	-	-	10	-	-	-	-
2,3-dichloro-1,3-butadiene	5	5	5	-	5	5	5	5
Disproportionated rosin acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Poly-p-styrene-sulfonic acid sodium salt*	-	-	0.1	0.5	0.5	0.5	1.0	5.0
Sodium styrene sulfonate	-	1.0	-	-	-	-	-	-
Oleic acid	-	-	-	-	1.0	2.0	-	-
Dodecyl mercaptan	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Water	100	100	100	100	100	100	100	100
Sodium hydroxide	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

* Degree of polymerization: 1000

Polymers I and II are comparison examples for chloroprene rubbers in which no polystyrene-sulfonic acid was used. Table 2, below, shows the values of the Mooney viscosity ML_{1+2} (at 100 °C) of the chloroprene rubber examples.

Table 2

Polymer number	I	II	III	IV	V	VI	VII	VIII
ML_{1+2} (at 100 °C)	64	60	60	65	67	65	65	64

Each of the chloroprene rubber examples listed by polymer number is mixed with the following substances on a 10-inch diameter roll at 50 °C:

Added substances	Proportion (in parts)
Rubber	100
Stearic acid	0.5
MgO	4
Carbon black (SRF)	40
Plasticizing oil	10
ZnO	5
2-mercaptoimidazoline	1

Each of the products is vulcanized in a different mold for 10 minutes at 220 °C in an unbroken series of 100. Table 3, below, shows the contamination of the metal molds after 100 vulcanizations.

Table 3

Polymer number	I	II	III	IV	V	VI	VII	VIII
Adhesion of the added substances	5	4-5	3-4	2-3	2	1-2	0-1	0-1

- 5 Pronounced adhesion over the entire surface
- 4 Marked adhesion over the entire surface
- 3 Moderate adhesion over the entire surface
- 2 Weak adhesion
- 1 Almost no adhesion
- 0 No adhesion

The added substances from polymers I and II produced in the comparison test show pronounced adhesion to the forms, so that the forms are distinctly contaminated by spots. As the results above show, though, addition of polystyrenesulfonic acid salt causes distinct reduction of the adhesion. Polymers VII and VIII are particularly noteworthy. No adhesion is noted with them, and the metal forms can be used for further tests without cleaning.

Example 2

Polymers of chloroprene monomer with other substances are produced, as shown in Table 4. Following polymerization, isolation and drying, the solid chloroprene rubber is produced in the same roll mill as in Example 1.

Table 4

Polymer number	IX	X	XI	XII	XIII	XIV	XV
Chloroprene	100	100	100	100	100	100	100
Potassium salt of disproportionated rosin acid	3.0	3.0	3.0	5.0	6.0	3.0	3.0
	-	1.0	1.0	1.0	1.0	1.0	1.0
Sodium salt of poly- α -methyl-p-styrenesulfonic acid with the degree of polymerization:	-	(n-10)	(n-50)	(n-50)	(n-50)	(n-100)	(n-100)
Sodium salt of α -methyl-p-styrenesulfonic acid	1.0	-	-	-	-	-	-
Dodecyl mercaptan	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Water	100	100	100	100	100	100	100
Sodium hydroxide	0.25	0.25	0.25	0.25	0.25	0.25	0.25

For comparison, a chloroprene rubber was produced without the sodium salt of poly- α -methyl-p-styrenesulfonic acid as Polymer No. IX, and a chloroprene rubber with a large addition of disproportionated rosin acid, beyond the region claimed, was produced as Polymer XIII. The Mooney viscosity ML_{1+1} (at 100 °C) for each of the example chloroprene rubbers produced is shown in Table 5, below.

Table 5

Polymer number	IX	X	XI	XII	XIII	XIV	XV
ML_{1+1} (100 °C)	54	53	50	54	50	53	52

Next, the chloroprene rubbers produced according to the polymer numbers above were mixed with the substances listed in Example 1 and the mixtures each were vulcanized 100 times, just as in Example 1. After the 100th vulcanization, the contamination of the metal form was determined visually, just as in Example 1. The values are shown in Table 6, below.

Table 6

Polymer number	IX	X	XI	XII	XIII	XIV	XV
Adhesion of the added substances	5	2-3	0-1	2-3	4-5	0-1	0-1

As the tests show, the chloroprene rubbers produced according to the invention are remarkably more effective in preventing metal form contamination than are the chloroprene rubbers at the state of the technology.